

# Chemical Communications

NUMBER 11/1966

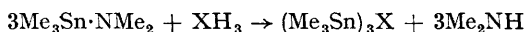
8 JUNE

## Shapes of Tris(trimethylstannyl)-amine, -phosphine, -arsine, and -stibine

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RECENT interest in the structures of  $(\text{H}_3\text{Si})_3\text{N}$ ,<sup>1</sup>  $(\text{H}_3\text{Si})_3\text{P}$ ,<sup>2</sup> and  $(\text{H}_3\text{Ge})_3\text{P}$ ,<sup>3</sup> has prompted us to investigate similar tin compounds. As it has not yet been possible to synthesise the derivatives  $(\text{H}_3\text{Sn})_3\text{X}$ , we have examined the corresponding trimethylstannyl compounds  $(\text{Me}_3\text{Sn})_3\text{X}$ , where  $\text{X} = \text{N}, \text{P}, \text{As}, \text{Sb}$ . These derivatives have been prepared in high yield by the reaction:



and have been characterised by elemental analyses and proton magnetic resonance spectroscopy (confirming the equivalence of 27 protons).

The vibrational spectra of these compounds have been investigated with a view to the possible determination of the shape of the  $\text{XSn}_3$  skeleton. For a pyramidal configuration having  $C_{3v}$  symmetry, the totally symmetric modes are active in both infrared and Raman spectra ( $A_1$  species are polarised, all other species must be depolarised), while in  $C_{3h}$  (planar skeleton, but no  $C_2$  axes or  $\sigma_v$  planes if the methyl groups are considered), the totally symmetric  $A'$  modes are active only in the Raman spectrum.

We have obtained infrared spectra (Perkin-Elmer 521, 4000—250  $\text{cm}^{-1}$  region) and Raman spectra (Perkin-Elmer L.R-1 using 6328 Å excitation with a sample of about 2 ml. in a multi-reflecting cell at 25—30°) of all the compounds in the liquid phase. Our results indicate that all the observed polarised Raman lines have equivalents in the infrared spectra. This clearly establishes that all the compounds are pyramidal, in spite of

the fact that Courtauld models allow construction of the nitrogen compound only in the planar configuration. For the nonplanar model to be correct, this suggests that the Sn-N bonds are unusually long, and therefore weak; an explanation consistent with the high reactivity observed for Sn-N derivatives.<sup>4</sup>

Our preliminary comparative analysis of the infrared and Raman spectra has enabled us to identify frequencies characterising the symmetric stretching modes of the  $\text{XSn}_3$  groups as highly polarised Raman lines at 514, 290, and 209  $\text{cm}^{-1}$  for the N, P, and As compounds respectively. In each of these pyramidal molecules, the symmetric stretching mode must involve motion of the central atom, so that without a complete normal-coordinate analysis (for which a knowledge of the out-of-plane angles is required), it is impossible to separate the mass effect from the effect upon these frequencies of changing Sn-X bond strength. Support for our assignment is provided by the occurrence at 322  $\text{cm}^{-1}$  of the analogous symmetric stretching mode in  $(\text{H}_3\text{Ge})_3\text{P}$ ,<sup>3</sup> but the corresponding  $\text{NSi}_3$  and  $\text{PSi}_3$  frequencies at 496 and 414  $\text{cm}^{-1}$  respectively,<sup>2</sup> are of little value for comparison since in these planar silyl compounds no motion of the central atom is involved. However, it is worth noting that the asymmetric stretching modes for these silicon compounds which do involve motion of the central atoms, occur at 987 and 455  $\text{cm}^{-1}$  respectively. This comparison suggests particularly weak Sn-N bonds in  $(\text{Me}_3\text{Sn})_3\text{N}$ , in keeping with our earlier conclusion.

The asymmetric stretching modes of the  $XSn_3$  skeletons are more difficult to assign with certainty, due to the depolarised and weak nature of their Raman lines, but detailed comparison of all our spectra indicates that these occur at 672,<sup>5</sup> 351, and 233  $cm^{-1}$  for the N, P, and As compounds respectively. The spectra of all compounds studied were essentially identical at frequencies above the 672  $cm^{-1}$  line, indicating that all other skeletal

modes give lower frequencies. The related Sn-N derivative,  $Sn(NMe_2)_4$ , appears to have its  $SnN_4$  asymmetric stretching mode at 538  $cm^{-1}$ , providing a further example of a low-frequency Sn-N stretching mode, though this evidently is at variance with a recent assignment<sup>6</sup> of the Sn-N stretch in *N*-trimethylstannylaniline at 843  $cm^{-1}$

(Received, April 21st, 1966; Com. 258.)

<sup>1</sup> E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, 1958, **13**, 202.

<sup>2</sup> G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Comm.*, 1965, 122, and *Spectrochim. Acta*, 1966, **22**, 67.

<sup>3</sup> S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Comm.*, 1965, 515.

<sup>4</sup> K. Jones and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 67, and references cited therein.

<sup>5</sup> K. Sisido and S. Kozima, *J. Org. Chem.*, 1964, **29**, 907, gave 728  $cm^{-1}$  as the  $\nu_{as}(Sn-N)$  from  $(Me_3Sn)_3N$ , but they had neither Raman spectra nor the analogous P and As compounds for comparison.

<sup>6</sup> E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1966, **1**, 109.